solution.[4] The solid which precipitated was removed by filtration and purified by crystallization from alcohol and water or benzene and petroleum ether.

Acknowledgment.—We wish to thank Dr. E. E. Reid for his interest and helpful suggestions in connection with this work.

DEPARTMENT OF CHEMISTRY
EMORY UNIVERSITY
EMORY UNIVERSITY, GEORGIA   RECEIVED MARCH 5, 1951

Anion Exchange of Zirconium, Hafnium, Niobium and Tantalum in Hydrochloric Acid Solutions

BY E. H. HUFFMAN, G. M. IDDINGS AND R. C. LILLY

The behavior of fluoride-containing complex ions of zirconium, hafnium, niobium and tantalum when eluted from anion exchange resins with mixtures of hydrochloric and hydrofluoric acids has been described and the nature of these ions has been discussed on several occasions.[1,2] It has been found in this Laboratory by the present writers and by D. A. Orth (for zirconium) that zirconium, hafnium, niobium and tantalum form complex chloro-ions in strong hydrochloric acid which can be exchanged on anion exchange resins. Some of the characteristics of these exchanges have been studied and are reported here.

Experimental

Radioactive tracers, with the exception of Zr[89], were obtained from the Isotopes Branch, U. S. Atomic Energy
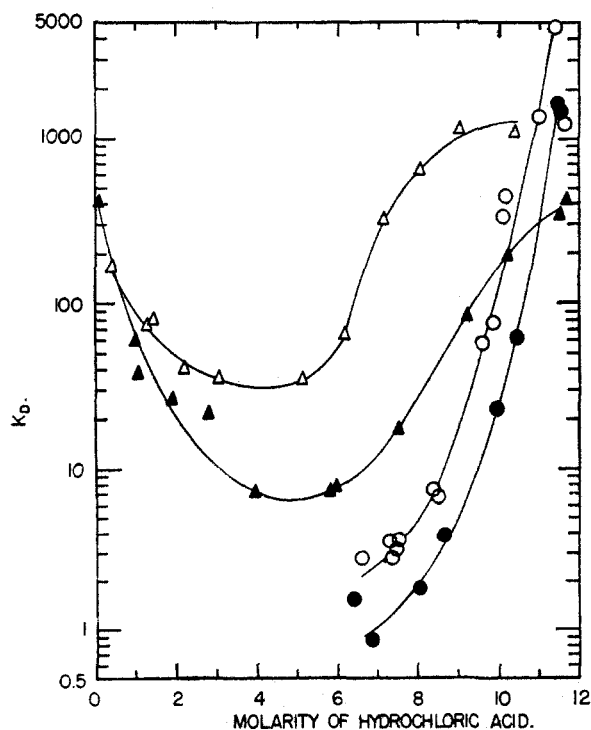

Fig. 1.—Dependence of the distribution coefficient at 25° on the hydrochloric acid concentration: △, niobium; ▲, tantalum; O, zirconium; ●, hafnium.

(1) K. A. Kraus and G. E. Moore, THIS JOURNAL, **71**, 3263, 3855 (1949); **73**, 9, 13 (1951).
(2) E. H. Huffman and R. C. Lilly. *ibid.*, **71**, 4147 (1949); **73**, 2902 (1951).

Commission. Zirconium tracer solutions were prepared from both Zr[95] and from Zr[89] produced by 100 mev. proton bombardment of niobium foil in the 184-inch cyclotron. The Zr[95] tracer was separated from the daughter Nb[95] by carrying the latter on precipitated manganese dioxide in a manner similar to that already reported.[3] This tracer in nitric acid was then combined with a weighed amount of zirconium dioxide and the whole converted to a solution in concentrated hydrochloric acid without other anions. The zirconium tracer for the batch equilibrations was prepared from Zr[89] (80 hr. half-life) in order to avoid interference from Nb[95] which would grow in if Zr[95] were used. It was chemically separated by the method of Hyde and O'Kelley,[4] and stored in concentrated hydrochloric acid. Hafnium tracer solutions in concentrated hydrochloric acid were prepared from hafnium dioxide containing Hf[181] and were about 0.003 molar in carrier hafnium. The Nb[95] tracer solutions were prepared from the material carried on the manganese dioxide in the Zr[95] purification. The small amount of Zr[95] activity which accompanied the Nb[95] was removed by extraction with thenoyltrifluoroacetone,[3] and the purified Nb[95] was finally made up in concentrated hydrochloric acid. An easier method for separating Zr[95] and Nb[95] was found during the course of this investigation and is reported below. This method was used for the separation in the later stages of the study.

The Ta[182] tracer was received in solution as potassium tantalate and contained carrier tantalum. About 0.2 ml. of this solution was heated with 1 ml. of concentrated hydrochloric acid containing a few drops of concentrated hydrofluoric acid. Evaporation to small volume, with added hydrochloric acid, was repeated several times to drive off hydrofluoric acid. The solution was then made up in 9 M hydrochloric acid and the activity was adsorbed on a column of Dowex-2 anion exchange resin to get rid of potassium. The Ta[182] activity was then washed from the column with 2 M hydrochloric acid. The activity of this solution compared to the specific activity of the original solution indicated the concentration of carrier tantalum to be about 1.2 micrograms per ml., or 7 × 10⁻⁶ molar.

The values of K_D at different hydrochloric acid concentrations were obtained by equilibrating 2.1–2.3 ml. of tracer solution with 15–300 mg. of 60–100 mesh Dowex-2 resin, oven-dried at 70°, in a plastic vial. The acid concentration of the solution was determined by titration after equilibration. The time required to reach equilibrium is discussed below. All equilibrations were made in a constant temperature bath at 25°.

The anion exchange separation of zirconium and hafnium was carried out by elution from the same resin with 9.0 M hydrochloric acid, using a lucite column 11 cm. in length and 6.5 mm. i.d., at a rate of 10–12 ml. per hour. A mixture of 3.8 mg. each of zirconium and hafnium, with tracers, in 1.2 ml. of concentrated hydrochloric acid was first adsorbed slowly at the top of the column for this purpose. Identification of the two peaks in the resulting elution curve
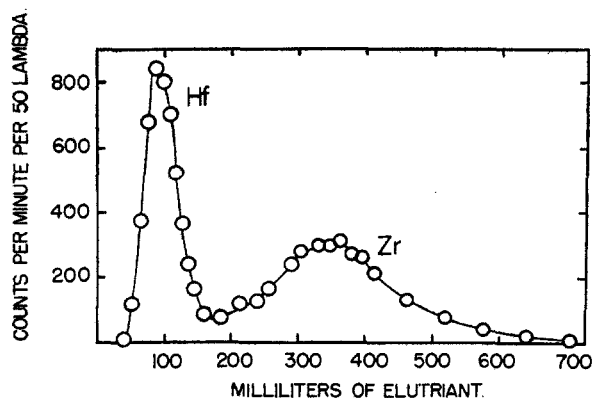

Fig. 2.—Elution of chlorozirconate and chlorohafniate with 9.0 M hydrochloric acid.

(3) R. E. Connick and W. H. McVey, *ibid.*, **71**, 3182 (1949).
(4) E. K. Hyde and G. D. O'Kelley, University of California Radiation Laboratory Report UCRL-1064 (December, 1950); accepted for publication in *Chem. Rev.*

was made both by the total count under each peak and by spectrographic analysis.

Discussion

The distribution coefficient is defined by the equation

$$K_D = \frac{M_r \times \text{volume of solution}}{M_1 \times \text{mass of resin}}$$

where M_r and M_1 are the fractions of the anion in the resin and the liquid phases, respectively. The dependence of K_D on the concentration of hydrochloric acid for the four elements is shown in Fig. 1, and a good separation of zirconium and hafnium by elution with 9.0 M hydrochloric acid is shown in Fig. 2. The order of elution is the reverse of that shown for the fluo-ions of these elements.[1,2] A small amount of Nb[95], which grew in from the Zr[95] decay, is still on the column at the end of this run.

The curves for the K_D values for niobium and tantalum are quite different from that for protactinium,[5] which they might be expected to resemble. Considerably more data with respect to several variables are needed to show the nature of the exchange in the high and low acid concentration ranges, though it is probable that there is little or no chloride complexing in the low concentrations. Zirconium and hafnium do not show similar behavior in the low acid concentrations.

Although the zirconium and hafnium batch experiments reach equilibrium within four hours and a good column separation can be achieved, the case is quite different for niobium and tantalum. It requires only four hours to reach equilibrium on the high acid side for the latter elements but at least two days on the low acid side of the curves; and neither niobium nor tantalum can be eluted from a column in a normal fashion with low acid concentrations, but are washed off immediately. In addition, tantalum does not behave normally when eluted from a column with 6–9 M hydrochloric acid after it has been adsorbed from 10–11 M acid. The tantalum concentration rises to an immediate peak and then falls off more slowly. It was first thought that the behavior of tantalum was due to the presence of the minute concentration of carrier present. However, a sample of carrier-free Ta[177] tracer, produced by deuteron bombardment of hafnium, gave the same results. This behavior does allow a good column separation from niobium, which shows a normal elution curve in this region.

The different characteristics of zirconium and niobium have led to a very convenient separation of Zr[95] from its daughter Nb[95]. The mixture in 1 ml. of 6–7 M hydrochloric acid is passed through a Dowex-2 column 8 cm. long and 3 mm. i.d. and washed with 3 more ml. of acid. The elutriant and wash contain the zirconium. The niobium is then washed from the column with about 4 ml. of 1.5–4.0 M hydrochloric acid.

Acknowledgments.—The spectrographic analyses for this study were made by John Conway and Milton Moore of this Laboratory. This work was done under the auspices of the U. S. Atomic Energy Commission.

(5) K. A. Kraus and G. E. Moore, THIS JOURNAL, **72**, 4293 (1950).

X-Ray Diffraction Study on the Structure of the Ni–Cu Coprecipitation Catalysts

BY NORIAKI KADOTA AND SADAAKI IKEDA

Both inhibitor and promoter actions are reported as to the influence of Cu on the catalytic activity of Ni catalysts. Copper acts as an inhibitor in Ni catalysts in the Fischer–Tropsch process, whereas in the case of ordinary hydrogenation it is often used as a promoter for Ni catalysts. The study of Ni–Cu coprecipitation by Morris and Selwood[1] suggests the possibility of the existence of a non-equilibrium alloy phase.

The X-ray structure of Ni–Cu catalysts coprecipitated from a mixture of their nitrate solutions on the surface of a kieselguhr carrier has been studied by the authors and a conclusion similar to that of Morris and Selwood obtained directly.

Experimental

Mixtures of nickel and copper nitrate solutions were coprecipitated by addition of K_2CO_3 solution on the kieselguhr surface. The precipitate was washed with hot water (94–96°). Impurities were spectroscopically detected and are as follows: chemicals: $Ni(NO_3)_2$; $Cu(NO_3)_2$; K_2CO_3; impurities: Ag(M), Co(M), Cu(M), Pb(W), Si(M); Na(W), Pb(W), Si(T), Ti(W); no trace of impurities, respectively, where M indicates medium, W weak and T traces, each referring to the intensity of the ultimate spectra lines. The amounts of impurities may be considered to be harmless.

Five kinds of catalysts were prepared, each containing 1.25 times as much kieselguhr by weight as the sum of Ni and Cu. These catalysts were reduced by hydrogen for about 90 hours at 300°. The results of the lattice measurements are shown in Table I, where the ratio of Ni to Cu corresponds to the atomic percentage of the two elements.

TABLE I

Compositions of catalysts Ni:Cu:KG			Lattice distances, Å. expected values	observed values	Additive composition from obsd. lattice dist. Ni	Cu
100	0	125	3.517[a]	3.517	100	0
95	5	125	3.521	3.517	100	0
70	30	125	3.545	3.529	88	12
50	50	125	3.565	3.547	67	33
				3.580	20	80[b]
50	50	125	3.565	3.577	37	63[c]
0	100	125	3.612[a]	3.612	0	100

[a] International Critical Tables. [b] Results after reduction for 10 hours. [c] Results after heat treatment for 90 hours.

A plot of lattice distance *versus* atomic fraction of the two metals is shown in Fig. 1. An S-shaped curve is found in spite of the expectation from the well-known Vegard's relationship in Ni–Cu alloy.[2] In particular, dual structures are observed in the equifractional sample of both metals, and they converge into a single structure after being heated for about 90 hours as shown schematically in Fig. 2. In Fig. 2, the rate constant from the initial structure of 3.547 Å. to the final structure of 3.577 Å. lattice distance is larger than the rate from the structure of 3.580 Å. spacing. This may be attributed to the difference in the rates of the mutual diffusion into each other between Ni and Cu (the rate of diffusion of Cu into Ni is 11 $\times$ 10^{-7} cm./day and that of Ni into Cu is 5 $\times$ 10^{-8} cm./day at 1000°).[3] With these results, we reach the con-

(1) H. Morris and P. W. Selwood, THIS JOURNAL, **65**, 2245 (1943).
(2) Sacklowski, Z. Physik, **5**, 21 (1921).
(3) Jenkin, "International Critical Tables," Vol. V, p. 76.